

Public Review Draft

**Analysis of the Air Quality Impacts of
the Use of Ethanol in Gasoline**

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I. Background

Governor Gray Davis issued Executive Order D-5-99 on March 25, 1999 calling for the removal of methyl tertiary-butyl ether (MTBE) from gasoline at the earliest possible date, but not later than December 31, 2002. Task 10 of the Executive Order states “the California Air Resources Board (ARB) and the State Water Resources Control Board (SWRCB) shall conduct an environmental fate and transport analysis of ethanol in air, surface water, and groundwater. The Office of Environmental Health Hazard Assessment (OEHHA) shall prepare an analysis of the health risks of ethanol in gasoline, the products of incomplete combustion of ethanol in gasoline, and any resulting secondary transformation products. These reports are to be peer reviewed and presented to the Environmental Policy Council by December 31, 1999 for its consideration.”

This report has been prepared in response to the Executive Order D-5-99. To assist OEHHA in its risk assessment, we conducted an analysis to estimate the changes in ambient air concentrations of potentially detrimental contaminants of exhaust and evaporative components and subsequent reaction products that would result from substituting ethanol-blended gasoline for gasoline blended with MTBE. We also included non-oxygenated gasoline in our analysis to provide some basis for comparison. The following sections summarize our estimates of volatile organic compound (VOC) emission profiles and emission inventories, modeling of air quality impacts, and data analysis of current and future air quality concentrations. Seven appendices contain detailed information. We evaluated emission and air quality impacts for the following four fuels:

- ◆ Current MTBE-based California Phase 2 Reformulated Gasoline (CaRFG).
- ◆ Ethanol-based fully complying fuel (with oxygen content of 3.5 wt%).
- ◆ Ethanol-based fully complying fuel (with oxygen content of 2.0 wt%).
- ◆ A non-oxygenated fully complying fuel.

We focused our analysis on the following air contaminants:

- ◆ Criteria air pollutants [carbon monoxide (CO), nitrogen dioxide (NO₂), ozone, and particulate matter (PM₁₀, PM_{2.5})].
- ◆ Toxic air contaminants (acetaldehyde, benzene, 1,3-butadiene, and formaldehyde).
- ◆ Fuel oxygenates (ethanol and MTBE).
- ◆ Alkylates [branched alkanes such as 2-methylpentane, 3-methylpentane, methylcyclopentane, and 2,2,4-trimethylpentane (“isooctane”)].
- ◆ Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN).
- ◆ Nitric acid (HNO₃).
- ◆ Additional compounds of interest to OEHHA (isobutene, toluene, xylene isomers, and *n*-hexane).

II. Automotive Emissions

A. VOC Speciation Profiles

We developed VOC speciation profiles for each fuel for the following processes and applied to all gasoline-related emission inventory categories (e.g., passenger cars, motorcycles, heavy-duty vehicles, fuel spillage, etc.):

- ◆ Start exhaust -- catalyst and non-catalyst.
- ◆ Hot stabilized exhaust -- catalyst and non-catalyst.
- ◆ Diurnal and resting evaporative.
- ◆ Hot soak and running evaporative.
- ◆ Liquid fuel.

For MTBE-blended CaRFG, we used VOC speciation profiles previously developed from ARB surveillance data and presented at a public workshop in September 1998.

We reviewed available data on VOC speciation from existing vehicle emission test programs to identify those that best represent the three fully complying non-MTBE fuels. These formed the basis for adjustments that can be applied to the VOC speciation profiles for the CaRFG base fuel. We developed the adjustments by comparing an emission profile for MTBE-blended CaRFG with a profile for an ethanol-blended or oxygen-free test fuel from the same study that was similar in hydrocarbon composition. The ethanol-blended test fuels were made with the same hydrocarbon bases as were the MTBE-blended fuels. However, to meet the Reid Vapor Pressure (RVP) limit in the CaRFG regulations, refiners that blend commercial fuels with ethanol will usually use modified hydrocarbon bases; most likely pentane content will decline and alkylates content will increase. (Aromatics and olefins will be constrained by the Predictive Model.) Such changes will not involve highly reactive species; so, data from splash-blended test fuels rather than commercial fuels should be adequate here with regard to reactivity.

Two following studies provided emission data contrasting MTBE-blended CaRFG with CaRFG blended with ethanol:

- ◆ The recent ARB testing of an MTBE-blended CaRFG and a fuel with high RVP and 10% ethanol.
- ◆ A test program sponsored by ARB in 1995, "Effects on Exhaust and Evaporative Emissions of Phase 1 and Phase 2 Gasolines", by Automotive Testing Laboratories (ATL).

In addition, "Auto/Oil" Technical Bulletin 17A provided the data for adjustments to approximate emissions from at least one type of oxygen-free CaRFG. In addition, we input properties of ethanol-blended and oxygen-free CaRFGs--predicted in a recent linear-program modeling study by MathPro sponsored by the California Energy Commission--into the ARB's Predictive Model for exhaust emissions of benzene and 1,3-butadiene and into newly created models for aldehyde emissions and evaporative benzene emissions.

In general, within each emission study, the VOC speciation profiles for the MTBE-blended test fuel are similar to those for the ethanol-blended or oxygen-free test fuel. In most cases, the only significant differences are the interchange (or removal of) the oxygenate and, for exhaust profiles, the interchange of the major partial combustion products of the oxygenates (e.g., formaldehyde and isobutene from MTBE, acetaldehyde from ethanol). The non-oxygenated fuel predicted by MathPro has a lower aromatic content than does the MTBE-blended CaRFG; the octane replacement for MTBE is provided by increased blending of alkylates. These changes result in lower ozone-forming potential, as calculated using the maximum incremental reactivities developed by Carter (1994). However, the exhaust profiles for non-oxygenated fuel have *higher* contents of C₈ and higher aromatic species and higher ozone-forming potential because all non-MTBE-related species were predicted to increase when MTBE is removed from the fuel. Based on vehicle emission test data, this would not be expected. Also, when removing MTBE, sulfur would have to be reduced. Lower sulfur would result in more efficient catalysts and lower exhaust hydrocarbon emissions and generally less reactive emissions. This issue is being further investigated from the perspective of both a further evaluation of engineering principles and a review of test data. This apparent discrepancy will be partially addressed by the gasoline headspace and vehicle emission testing described in Section II.D.

The profiles from the MTBE-blended test fuels are usually similar (in some cases, identical) to the current ARB profiles adopted last year. Therefore, the differences between profiles within the test studies can be applied with some confidence to adjust the VOC speciation profile for the CaRFG base fuel. However, each study referenced earlier has limitations that complicate its use. The Auto/Oil work did not measure extended diurnal emissions. None of the studies used non-catalyst vehicles. The evaporative data from ARB's MTBE-ethanol test program have excessively high *n*-butane, due to the manner in which the carbon canisters were prepared. The ATL data do not include alcohols or

aldehydes, which are the most important contrasting species between emissions from MTBE- and ethanol-blended fuels. (However, surrogate aldehyde data are available.) As splash-blended test fuels, the ethanol-blended fuels do not exactly reflect commercial fuels. Also, they were not true CaRFGs. (The ethanol-blended fuels did not meet the RVP limit at 7 psi. Also, they did not completely satisfy the Predictive Model. In particular, the ARB ethanol-blended fuel had a high oxygen content that caused a high NO_x prediction.) Finally, the ATL work did not include speciation of the gasolines, so that its emission profiles cannot be related to its gasoline compositions.

Although not perfect representations, the compositions of the comparison fuels used in this analysis generally conform to statements from refiners about how they would have to change their gasolines to meet the CaRFG regulations with ethanol. The changes include significant removal of pentanes and an increased use of alkylates.

B. Peer Review

Professor Robert Harley of the University of California at Berkeley peer reviewed the VOC speciation profiles, and calculated headspace vapors from the liquid fuel speciation profiles as a check on the ones developed in-house. Professor Harley suggested that the headspace evaporative VOC emission profiles (used to represent diurnal evaporative emissions) developed by ARB staff for the two ethanol-blended gasolines (2.0 and 3.5 wt% oxygen) may be too high in ethanol emissions and, as a result, too low in emissions of other species. Also, he suggested that the liquid gasoline composition be used as an alternate representation for hot soak vapors. The liquid gasoline has much higher alkane content than ARB's hot soak emissions. This results in lower content of all other gasoline components, especially toluene and ethanol. Thus, the overall result of using Professor Harley's profiles are to reduce the amount of ethanol emissions. We implemented these recommendations by performing photochemical grid model simulations for both the ARB evaporative profiles and those recommended by Professor Harley. His recommended profiles are designated with a trailing "H" in subsequent tables. This approach serves to bracket the range of uncertainty in the ethanol content of the VOC speciation profiles.

C. Mass Emissions

We estimated total mass emissions of VOC, oxides of nitrogen (NO_x), and CO for CaRFG using the current mobile source emissions model, MVEI7G. Stationary source emissions were assumed to be the same for all scenarios. For the three fully complying non-MTBE fuels, the Predictive Model constrains the total mass emissions of VOC and NO_x.

Based on several vehicle emission test programs and ambient air studies (Dolislager, 1997), CO emissions decrease with increasing fuel oxygen content. For the purpose of this evaluation, we used the same motor vehicle CO inventory for the MTBE and ethanol fuel scenarios with 2% oxygen content, and increased CO emissions by 5% for the non-oxygenated scenario and decreased CO emissions by 15% for the ethanol 3.5% oxygen scenario. The CO emission inventory has a small impact on concentrations of ozone and other secondary pollutants. Since CO is not considered a toxic compound in the context of this study, the CO concentrations simulated for each scenario are not part of any further analysis.

It should be noted that a substantial portion of the CO reductions that can be attributed to CaRFG comes from properties of the fuel other than the oxygen content. This means that addition or removal of oxygen in CaRFG is likely to have less impact on CO emission than its use in non-RFG wintertime blends.

The resulting emission inventories for the South Coast Air Basin (SoCAB) are shown in Tables 1 to 3 for CO, NO_x, reactive organic gases (ROG), benzene, 1,3-butadiene, acetaldehyde, formaldehyde, ethanol, and MTBE. Table 1 summarizes the total emissions (mobile, area, stationary, and natural

sources) for an average ozone episode day for the seven fuel scenarios. Table 2 and 3 present emission changes relative to the 1987 and 2003 baselines, respectively.

D. Vehicle Emission Testing

In order to determine if the VOC speciation profiles for the three fully complying non-MTBE fuels are reasonable, we are conducting complete exhaust VOC speciation tests for multiple vehicles using two prototype non-MTBE regular-grade gasolines currently being produced and sold commercially in California. One is an non-oxygenated gasoline produced by Chevron and the other is a gasoline blended by Tosco with ethanol at a 2.05 wt% oxygen content. Both fuels fully comply with California's current CaRFG regulations. We are also speciating the liquid fuels and headspace vapors. We anticipate that full-scale production of fully complying non-MTBE gasoline will result in blends different from those being produced today. However, we expect the results from these tests to yield valuable insights into the directional effects of using ethanol-blended and non-oxygenated gasolines. This will provide a reality check for the profiles prepared in-house and by Professor Harley using limited test data.

III. Photochemical Modeling

A. Model Description

We applied the Urban Airshed Model with the Flexible Chemical Mechanism interface (UAM-FCM) for the August 26-28, 1987 ozone episode in the SoCAB. Input files for winds, temperature, and diffusion break were developed using special air quality and meteorological data collected during the 1987 Southern California Air Quality Study (Lawson 1990). We simulated initial and boundary conditions, together with emission inventories for calendar years 1997 and 2003 using the meteorology from the 1987 episode. Fixing the meteorological conditions in this way allows the effects of fuel changes to be directly calculated. We used an extended version of the SAPRC-97 photochemical mechanism (Carter et al., 1997) to simulate atmospheric chemical transformations. The mechanism includes explicit treatments of the chemistry for the criteria pollutants, acetaldehyde, benzene, 1,3-butadiene, ethanol, formaldehyde, HNO_3 , MTBE, PAN, and PPN. The mechanism tracks secondary formation of acetaldehyde and formaldehyde separately from the contribution of direct emissions. SAPRC-97 lumps the alkylates, isobutene, toluene, xylene isomers, and *n*-hexane with similarly reactive compounds, so we estimated upper-limit concentrations based on analysis of ambient air quality measurements (see Section IV.B.6). OEHHA determined that the upper-limit concentrations for isobutene, toluene, xylene isomers, and *n*-hexane were an order of magnitude below any level of concern, so there was no need to treat these compounds explicitly in the photochemical modeling. OEHHA is still evaluating levels of concern for the alkylates.

To establish baseline conditions, we simulated 1997 mass emissions with the VOC speciation profiles for CaRFG. Calendar year 2003 was evaluated for CaRFG and the three fully complying non-MTBE fuels plus the two Harley emission scenarios. We assumed boundary conditions to vary from 1987 concentrations consistent with the emission inventory. However, initial concentrations are invariant. Model results for the first and second days of the simulation are greatly influenced by the initial conditions for ozone and its precursors. Therefore, only the results for the third day (i.e., August 28) of the simulations are reported.

B. Results

For all seven scenarios, we processed UAM-FCM results for the peak one-hour-average, 8-hour-average (CO and ozone only), and 24-hour-average concentrations for all compounds of interest. Table 4 compares the changes in population-weighted 24-hour-average pollutant

concentrations between the 1997 CaRFG base fuel and the six 2003 fuel scenarios to give the reader a quick sense of temporally and spatially integrated patterns across the modeling domain. Most pollutants show decreases from the 1997 baseline to the 2003 baseline (“2003-MTBE”) due to reductions in overall emissions. The predicted decreases are especially pronounced for the toxic air contaminants, ranging from 13% for formaldehyde and acetaldehyde to 43% for 1,3-butadiene. The domain peak one-hour-average ozone is estimated to decrease about 1 part-per-hundred-million (approximately 5%) between 1997 and 2003 (see Table 6).

Table 5 compares the changes in population-weighted 24-hour-average pollutant concentrations between the 2003 baseline and the five 2003 MTBE-free fuel scenarios. Since fuel-related activities are the only inventoried source of MTBE, concentrations fall to zero. Benzene (0 to -9%), formaldehyde (-1 to -2%), and NO₂ (0 to -1%) concentrations stay the same or decrease for all the fuel scenarios. As expected, the non-oxygenated gasoline results in higher predicted CO concentrations (2%) and the 3.5 wt% oxygen ethanol-blend in lower CO values (-7%). Also, as expected, acetaldehyde (1 to 6%) and ethanol (37 to 121%) concentrations increase for the ethanol-blended fuels. These changes in acetaldehyde and ethanol are predicted to lead to increases in PAN concentrations (1 to 3%) that are no different than those predicted for the non-oxygenated gasoline (3%). Changes to 1,3-butadiene (-2 to 2%) and PPN (-1 to 4%) are similarly modest for all the fuel scenarios.

We investigated the lack of sensitivity of PAN formation to ethanol-blended fuels by tripling motor vehicle hydrocarbon and CO emissions for the 1997 baseline, the 2003 ethanol-blended fuel with 3.5 wt% oxygen content using Professor Harley's VOC speciation profiles, and the 2003 non-oxygenated fuel. Increasing the hydrocarbon-to-NO_x ratio by this amount should significantly increase radical concentrations and speed the photochemical processes that lead from acetaldehyde and ethanol to PAN. The factor of three increase in motor vehicle emissions is much larger than that expected in the soon-to-be-released EMFAC99 version of California's on-road motor vehicle emission model (Mark Carlock, personal communication) and from the results of a 1997 fuel-based emission inventory for the SoCAB (Singer and Harley, 1999), but serves to allow insight into expected impacts if the motor vehicle inventory increases dramatically. As an example of why we consider this to be an upper-bound, peak one-hour-average ozone concentrations were predicted to be 0.422 ppm, well above the 0.244 ppm peak value actually observed in the SoCAB between 1996 and 1999. Peak acetaldehyde concentrations increased by 64% and PAN concentrations by 178% for the ethanol-blended fuel. However, these increases were very similar to those predicted for the non-oxygenated fuel for acetaldehyde (59%) and PAN (175%). Thus, we conclude that increases in acetaldehyde and ethanol emissions will not lead to substantially high PAN concentrations, presumably because other VOCs are larger contributors to PAN formation.

Among the 2003 MTBE-free fuel scenarios, domain peak one-hour-average ozone ranges from 0.2201 to 0.2242 ppm for the ethanol-blended fuels to 0.2266 ppm for the non-oxygenated fuel. The predicted 0.0037 ppm (1-2%) increase in ozone above the 2003 baseline by the non-oxygenated fuel appears to be due to the assumed increases in exhaust emissions of C₈ and higher aromatic species, as well as CO. The results of sensitivity simulations indicate that about two-thirds of the increase is due to the aromatics and one-third to the CO. Recall from Section II.A that there is substantial uncertainty about the higher aromatic content of the exhaust since the aromatics in the fuel are predicted to be *lower*. This issue is under evaluation and will be investigated further in the vehicle emission testing described in Section II.D.

The peak 24-hour-average HNO₃ concentration decreases by 12% from 1997 to 2003. Among the 2003 fuel scenarios, the largest HNO₃ concentration increase is about 0.1%. Thus, PM₁₀ and PM_{2.5} concentrations are not expected to change appreciably as a result of the introduction of MTBE-free fuels.

IV. Ambient Air Quality

A. Findings of Previous Studies

As part of our evaluation of the potential air quality impacts of substituting ethanol-blended gasoline for MTBE-blended gasoline, we conducted a literature review of related programs implemented elsewhere. Ethanol has been a major component of light-duty vehicle fuels in several states in the United States including Alaska, Arizona, Colorado, and New Mexico. In Brazil, either neat (100%) ethanol or gasohol (a mixture of ethanol and gasoline) has been used as a fuel since 1979.

A total of sixteen papers and reports were reviewed, of which nine provided information pertinent to the situation in California. The remaining studies were not as useful because they did not include a before-and-after study or they did not include ambient air quality impacts. The studies of the impact of the use of ethanol fuel on air quality conducted in Denver, Albuquerque, and Brazil provided the most useful insights. The primary focus of these studies was on the change in ambient concentrations of acetaldehyde and PAN.

1. Denver, Colorado

The Denver metropolitan area is the first region in the United States to implement the use of oxygenated fuel in an effort to reduce ambient carbon monoxide (Anderson et al., 1994). The program has been mandated since the beginning of 1988 when the majority of the fuel sold contained 8% MTBE with the rest being a 10% ethanol blend. Since then, the additive used has gradually shifted from largely MTBE to largely ethanol. Anderson et al. (1997) reported that the concentrations of formaldehyde and acetaldehyde during the winter of 1995/96, when nearly all of the fuel was blended with ethanol, were not significantly different from those measured during the winter of 1988/89 when 95% of the fuel was blended with MTBE. They concluded that photochemical production and destruction of these carbonyl compounds suppress the emissions effect.

2. Albuquerque, New Mexico

Albuquerque is one of the U.S. urban areas mandated to use oxygenated gasoline fuel blends for improving air quality during the winter months. In the winter, over 99% of the fuel sold contains 10% ethanol. Gaffney et al. (1997) examined the air quality impacts of ethanol-gasoline fuel blends by measuring the ambient concentrations of PAN and aldehydes in the summer of 1993 (prior to the introduction of ethanol-blended fuel) and in the winters of 1994 and 1995 (after the introduction of ethanol-blended fuel). Compared to the summertime data, they observed a 10% acetaldehyde increase during one winter, but a significant decrease (lower by a factor of five) in the other winter. The study observed an increase of PAN by a factor of two and four, respectively, in both winters which the authors attributed to the use of ethanol fuel. However, as pointed out by Whitten (1998), the study conducted by Gaffney et al. (1997) is not a convincing case for demonstrating the air quality impact of ethanol fuel. The major arguments are the lack of control conditions (i.e., no data for pre-ethanol wintertime conditions) and meteorological variation. For example, average concentrations of PAN varied by a factor of two between the two winters, largely due to meteorology.

3. Brazil

Brazil is the only country in the world where a national, large-scale ethanol fuel program has been implemented. The ethanol fuel was first introduced in 1979 and its use has increased steadily since then. In 1997, approximately nine million automobiles in Brazil ran on a gasohol fuel (22% ethanol-blended fuel) and another four million ran on neat ethanol (Grosjean 1997). Grosjean et al. (1990) measured ambient concentrations of aldehydes in three major urban cities

of Brazil: San Paulo, Rio de Janeiro, and Salvador from 1986 to 1988 and reported that acetaldehyde was the most abundant carbonyl in terms of its peak concentration (35 ppb), followed closely by formaldehyde (34 ppb). The results also showed that acetaldehyde concentrations in urban areas of Brazil were substantially higher than those measured elsewhere in the world, most likely caused by large-scale use of ethanol as a vehicle fuel. In contrast, the ambient concentrations of formaldehyde showed a small increase compared to those measured elsewhere. More recently, de Andrade et al. (1998) reported that the concentrations for formaldehyde and acetaldehyde measured in Salvador, Brazil ranged from 0.20 to 80 ppb and from 0.40 to 93 ppb, respectively. Because of high concentrations of ambient acetaldehyde, Tanner et al. (1988) observed up to 5 ppb of PAN. Since there were no ambient data available prior to the use of ethanol fuel, these studies could not evaluate the direct impact on air quality before and after the use of ethanol fuel.

B. Current and Future Air Quality

OEHHA requested peak 1997 and 2003 concentrations for the appropriate averaging times for the criteria air pollutants, and peak one-hour-average and 24-hour-average, as well as population-weighted annual-average concentrations, for all others. We provided 1997 baseline concentrations for alkylates, isobutene, toluene, xylene isomers, and *n*-hexane. OEHHA determined that the upper-limit 1997 concentrations for the latter four compounds are an order of magnitude below any level of concern, so there was no need to establish 2003 concentrations (which require photochemical modeling). OEHHA is still evaluating levels of concern for the alkylates. Analyses were only done for the SoCAB, the most populated and most polluted air basin in California. This is also the area in California (and perhaps the world) with the most air quality data, speciated VOC and toxic air contaminants in particular.

Ambient air quality data for criteria pollutants in 1996-1998 were used to represent the 1997 baseline to account for natural year-to-year meteorological fluctuations. Only 1996-1997 toxics data were used to represent the 1997 baseline since 1998 data were not readily available at the time of the analysis. Data from before 1996 were not used because fuels used then did not satisfy the CaRFG requirements. We used data from the following sources:

- ◆ 1996-1998 Criteria Pollutant Monitoring Network in the SoCAB.
- ◆ 1996-1997 ARB Toxic Air Contaminant Network in the SoCAB ("TAC data").
- ◆ 1996 SoCAB VOC Monitoring Study by Desert Research Institute ("DRI data").
- ◆ 1996 Desert Research Institute Sepulveda Tunnel Study.
- ◆ 1996 and 1997 UC Berkeley Caldecott Tunnel Studies.
- ◆ 1997 ARB Emission Inventory for the SoCAB.

Data from the 1997 Southern California Ozone Study and Multiple Air Toxics Exposure Study II data were not readily available at the time of our analysis. Although we originally proposed to include data from a 1999 UC Berkeley Tunnel Study conducted in July, these data were not available at the time of our analysis.

The photochemical modeling results were used to establish future air quality concentrations. For estimating future peak one-hour-average and 24-hour-average concentrations, we normally used the peak concentrations in the gridded modeling region for the third day of the model simulation. For the population-weighted annual-average exposure estimates, we normally used the region-wide population-weighted average of the daily-average model results.

1. CO, NO₂, Ozone, PM₁₀, PM_{2.5}

We used peak concentrations observed in 1996-1998 to represent the 1997 baseline and scaled them to 2003 with the photochemical modeling results. The predicted concentrations for the 1997 MTBE baseline, the 2003 MTBE baseline, the 2 wt% oxygen content ethanol blended fuel

(“Et2%”), the 3.5 wt% oxygen content ethanol blended fuel (“Et3.5%”), and the non-oxygenated fuel (“nonOxy”) are reported in Table 6. As described in Section III.B, PM10 and PM2.5 are not expected to change as a result of the MTBE phase-out.

2. Acetaldehyde, Benzene, 1,3-Butadiene, and Formaldehyde

We used two different approaches to estimate 1997 benzene and 1,3-butadiene concentrations. First, we used measured concentrations directly from the TAC sampling network. In addition, we used least-squares linear regression (forced through the origin after accounting for background concentration) to develop ratios between these toxic air contaminants and CO. We found good correlations with CO for benzene and 1,3-butadiene. We used the regression results to estimate concentrations at locations where there are no direct TAC measurements, but there are CO measurements. The latter approach allowed us to estimate pollutant concentrations at nineteen locations, rather than the five locations for which toxics sampling data are available. Model results for benzene and 1,3-butadiene were used to extrapolate from the 1997 base year to the various 2003 scenarios. The range of estimates developed using the different approaches are given in Table 6.

We considered three different approaches to estimate 1997 acetaldehyde and formaldehyde concentrations. First, we used measured concentrations directly from the toxics sampling network. Second, to derive peak one-hour-average concentrations from 24-hour-average measurements, we used the corresponding ratio for ozone. Third, we attempted to develop relationships between aldehydes and both CO and total oxidant (sum of ozone and NO₂) so aldehyde values could be estimated at many more locations than are sampled with the TAC monitoring network. Our attempt to correlate aldehydes with CO and oxidant was not considered sufficiently reliable and was abandoned.

Future year maximum one-hour and daily acetaldehyde and formaldehyde estimates were extrapolated from 1997 using modeled results for total acetaldehyde and total formaldehyde. To estimate future year population weighted exposure, we first split 1997 estimates into primary and secondary components and applied model results to extrapolate each component separately. The separate components were then added to obtain total acetaldehyde and total formaldehyde. Table 6 reports the range of estimates developed using all except the correlation method.

3. Ethanol and MTBE

The only ethanol air quality data readily available were those collected by DRI in the summers of 1995 and 1996. We used the 1996 data as the basis for estimating representative concentrations for 1997. The highest ethanol concentrations are expected in winter. Given only summer data, it was challenging to estimate concentrations in a different season. We opted to use CO as an index of mixing and dispersion to extrapolate from measured peak ethanol concentrations in the summer to a different season. The results are reported in Table 6. Similar to other pollutants, we attempted to correlate ethanol with CO, but results were poor. This was not surprising, given that on-road vehicles currently emit less than 1% of the estimated ethanol emissions in the SoCAB.

We used the two approaches described above for benzene and 1,3-butadiene to estimate MTBE concentrations. We found good correlations with CO for some datasets and not others. A range in estimates is given in Table 6.

4. Alkylates

Based on the measurements by DRI in the SoCAB in 1996, there were over 30 alkylates observed in the atmosphere. The top four alkylates in terms of their average concentration were 2-methylpentane (2.11 ppb), 3-methylpentane (1.24 ppb), methylcyclopentane (1.33 ppb), and

2,2,4-trimethylpentane (1.31 ppb). We used the DRI data and measured CO concentrations in 1996-1998 to estimate annual-average and peak one-hour-average alkylates concentrations, using a procedure similar to that used for isobutene and n-hexane. We developed ratios between the compounds of interest and CO. Both DRI data and Sepulveda Tunnel data were used in our analysis, as alkylates are not measured in the TAC monitoring network. Good correlation was observed for all four compounds for both datasets. The calculated 1997 peak one-hour-average concentrations range from 16 to 38 ppb. The corresponding annual-average concentrations are 1.7 to 4.2 ppb.

5. PAN and PPN

PAN and PPN have no direct sources and form *in situ* in the atmosphere. PAN has been measured earlier and more frequently in the SoCAB than anywhere else in the world (about 25 studies that span some 35 years). The highest PAN concentrations were recorded during early studies (and often outside the smog season), e.g. 60-65 ppb in the late 1960s. Many of the subsequent studies lasted only a few days, weeks, or months, thus providing us with no consistent basis to assess long-term trends. High concentrations of PAN (40 ppb or more) have been recorded until about 1980, and concentrations of PAN appear to have decreased substantially thereafter. No PAN concentration higher than 10 ppb has been reported since 1991. Consistent with the downward trend observed for peak one-hour-average PAN concentrations, 24-hour-average PAN concentrations have declined from 15-20 ppb in the late 1960s and until 1980, to 5-12 ppb in 1985-1990 and 2-5 ppb in 1993. Seasonal variations of PAN are sparsely documented, especially so in the last decade (no data since 1987). Results from earlier studies indicate that high concentrations of PAN were often recorded outside of the traditional smog season, and that coastal and central regions of the SoCAB may experience higher concentrations of PAN during the late fall than during the summer months. However, even though PAN has not been monitored routinely over a long period, many special studies demonstrate a downwind trend on average.

Ozone data can be used to predict the time of peak PAN but not to estimate PAN concentrations and their diurnal, seasonal, and spatial variations. It appears that thermal decomposition of PAN may account for much of the differences between diurnal, spatial, and seasonal variations of ambient PAN and those of ambient ozone.

Even less information is available for PPN than for PAN. Ambient concentrations of PPN have been reported in only nine studies. The highest concentrations of PPN were up to 5-6 ppb in earlier studies and 1 ppb or less in recent years. Twenty-four-hour-average concentrations range from 0.1 to 1.8 ppb. There are no data on seasonal variations or annual averages. Diurnal variations of ambient PPN are closely related to those of PAN. The slopes of the linear regressions of ambient PPN versus ambient PAN at all locations studied in 1993 and 1997 range from 0.10 to 0.17 (average = 0.15). These values may serve as a baseline when using the PPN-to-PAN concentration ratio as an indicator of the possible impact of replacing MTBE by ethanol on future PAN air quality in the SoCAB.

6. Isobutene, Toluene, Xylene Isomers, *n*-Hexane

OEHHA requested information on population-weighted annual average and peak one-hour-average concentrations for toluene, xylenes, isobutene, and n-hexane. In response to this, we did a sensitivity evaluation of 1997 concentrations for these compounds. The TAC network measures toluene and the xylene isomers (*meta*- and *para*-xylene, *ortho*-xylene) at five sites in the SoCAB. Thus, a key part of the sensitivity evaluation involved developing ratios between the compounds of interest and CO, as described for the alkylates. In general, we observed good correlation with CO for all compounds for all but a few datasets.

After reviewing the estimated 1997 concentrations relative to chronic Reference Exposure Levels (RELs), OEHHA concluded that even a few-fold difference in concentration from the use of one fuel over the other is not going to be a significant health concern. This was because current concentrations of these compounds are one to two orders of magnitude below their chronic RELs. The replacement of MTBE with hydrocarbons could not reasonably produce anything approaching this type of effect. Thus, airshed modeling analysis was not performed to assess future air quality concentrations of these compounds.

V. Recommendations for Additional Studies

In the absence of more precise description of production fuels once MTBE can no longer be used, the airborne environmental fate and transport analysis of ethanol-containing gasoline relies on engineering judgement which should not be viewed as definitive. This analysis should be revisited as additional information is gained on replacement fuels and their likely emission byproducts.

Our analysis of ambient air quality impacts should be confirmed with field measurements that take place before and after the planned December 31, 2002 phase-out of MTBE. California existing ambient air quality networks should be sufficient for all the criteria pollutants, MTBE, toxic air contaminants, and individual VOC compounds (i.e., alkylates). However, ethanol and PAN are not part of any routine air monitoring program.

Later this year, we will start a PAN and PPN monitoring program at two sites in the SoCAB. We are determining the feasibility of measuring ethanol. During the 1987 Southern California Air Quality Study, high PAN concentrations were observed at coastal sites (up to 19 ppb) during the winter and at Claremont (up to 30 ppb) during the summer. Therefore, year-around monitoring is warranted. For future monitoring, Burbank or downtown Los Angeles are candidates for a coastal site and Azusa is a good choice for an inland site because of existing MTBE and aldehyde measurements made as part of the TAC and Photochemical Assessment Monitoring Stations programs. Historic NO to NO₂ ratios and ozone and aldehyde concentrations will be examined before making a final selection. Since ethanol and acetaldehyde lead to PAN but not to PPN, the PPN-to-PAN ratio may be a useful indicator of the impact of ethanol on PAN air quality.

In 2000, we hope to fund year-around PAN, ethanol, aldehyde, MTBE, and possibly acetic acid measurements in the San Francisco Bay Area and the Central Valley as part of the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) and 2000 Central California Ozone Study (CCOS2000) field measurement programs.

VI. References

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Tables

Table 1	South Coast Air Basin Emissions, Tons/Day								
Year / Scenario	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
1997 Baseline Inventory (MTBE)	5440	1083	1037	17.83	3.46	6.78	21.71	33.55	31.15
2003 Baseline Inventory (MTBE)	4295	851	895	13.14	2.59	6.00	18.89	32.09	21.87
2003 Ethanol Blend at 2% Oxygen	4295	851	893	12.89	2.61	6.31	18.64	50.88	0.01
2003 Ethanol Blend at 3.5% Oxygen	3810	851	894	13.23	2.55	7.79	18.41	69.32	0.01
2003 Non-Oxygenated Fuel	4457	851	893	12.67	2.65	6.01	18.53	31.94	0.01
2003 Ethanol Blend at 2% Oxygen, Harley Version	4295	851	893	11.76	2.61	6.31	18.64	43.39	0.01
2003 Ethanol Blend at 3.5% Oxygen, Harley Version	3810	851	894	11.98	2.55	7.78	18.41	53.46	0.01

Table 2	Emission Changes from 1997 Baseline, Percent								
Scenario	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
2003 Baseline Inventory (MTBE)	-21%	-21%	-14%	-26%	-25%	-12%	-13%	-4%	-30%
2003 Ethanol Blend at 2% Oxygen	-21%	-21%	-14%	-28%	-25%	-7%	-14%	52%	-100%
2003 Ethanol Blend at 3.5% Oxygen	-30%	-21%	-14%	-26%	-26%	15%	-15%	107%	-100%
2003 Non-Oxygenated Fuel	-18%	-21%	-14%	-29%	-23%	-11%	-15%	-5%	-100%
2003 Ethanol Blend at 2% Oxygen, Harley Version	-21%	-21%	-14%	-34%	-25%	-7%	-14%	29%	-100%
2003 Ethanol Blend at 3.5% Oxygen, Harley Version	-30%	-21%	-14%	-33%	-26%	15%	-15%	59%	-100%

Table 3	Emission Changes from 2003 Baseline (MTBE), Percent								
Scenario	CO	NOx	ROG	Benzene	Butadiene	Acetaldehyde	Formaldehyde	Ethanol	MTBE
2003 Ethanol Blend at 2% Oxygen	0%	0%	0%	-2%	1%	5%	-1%	59%	-100%
2003 Ethanol Blend at 3.5% Oxygen	-11%	0%	0%	1%	-1%	30%	-3%	116%	-100%
2003 Non-Oxygenated Fuel	4%	0%	0%	-4%	2%	0%	-2%	0%	-100%
2003 Ethanol Blend at 2% Oxygen, Harley Version	0%	0%	0%	-10%	1%	5%	-1%	35%	-100%
2003 Ethanol Blend at 3.5% Oxygen, Harley Version	-11%	0%	0%	-9%	-1%	30%	-3%	67%	-100%

Table 4						
	Changes in Gridded Region Summer Pop. Wt. Daily Avg. from 1997 Baseline, Percent					
Pollutant Name	2003-MTBE	2003-ET20	2003-ET20H	2003-ET35	2003-ET35H	2003-UNOX
Acetaldehyde (Primary)	-26%	-22%	-21%	4%	4%	-26%
Acetaldehyde (Secondary)	-12%	-10%	-11%	-9%	-11%	-11%
Acetaldehyde (Total)	-13%	-11%	-12%	-8%	-10%	-12%
Benzene	-27%	-28%	-33%	-26%	-32%	-29%
Butadiene	-43%	-43%	-43%	-44%	-44%	-42%
CO	-18%	-18%	-18%	-24%	-24%	-16%
Ethanol	-5%	51%	30%	109%	63%	-6%
Formaldehyde (Primary)	-25%	-26%	-26%	-27%	-27%	-27%
Formaldehyde (Secondary)	-11%	-12%	-12%	-11%	-12%	-12%
Formaldehyde (Total)	-13%	-14%	-15%	-14%	-14%	-14%
MTBE	-32%	-100%	-100%	-100%	-100%	-100%
NO	-46%	-46%	-46%	-46%	-46%	-47%
NO2	-28%	-28%	-28%	-28%	-28%	-28%
PAN	-3%	-1%	-3%	-1%	-3%	-1%
PPN	-1%	0%	0%	-2%	-2%	3%
Table 5						
	Changes in Gridded Region Pop. Wt. Summer Daily Avg. from 2003 MTBE Baseline, Percent					
Pollutant Name	2003-ET20	2003-ET20H	2003-ET35	2003-ET35H	2003-UNOX	
Acetaldehyde (Primary)	5%	6%	39%	40%	0%	
Acetaldehyde (Secondary)	2%	1%	3%	2%	1%	
Acetaldehyde (Total)	2%	1%	6%	4%	1%	
Benzene	-2%	-9%	0%	-7%	-3%	
Butadiene	0%	0%	-2%	-2%	2%	
CO	0%	0%	-7%	-7%	2%	
Ethanol	59%	37%	121%	72%	-1%	
Formaldehyde (Primary)	-2%	-2%	-3%	-3%	-2%	
Formaldehyde (Secondary)	-1%	-2%	-1%	-2%	-1%	
Formaldehyde (Total)	-1%	-2%	-1%	-2%	-1%	
MTBE	-100%	-100%	-100%	-100%	-100%	
NO	-1%	0%	0%	1%	-2%	
NO2	-1%	-1%	-1%	0%	-1%	
PAN	3%	1%	2%	1%	3%	
PPN	2%	1%	-1%	-1%	4%	

Table 6							9/23/99	
Range of Estimated Maximum Pollutant Levels for Various Scenarios								
South Coast Air Basin								
			Year / Scenario					
Pollutant / Avg. Type	Estimate		1997	2003	2003	2003	2003	
	Type		MTBE	MTBE	Et2%	Et3.5%	NonOxy	
Benzene, ppb								
	Population Weighted Annual Exposure							
	Upper		1.19	0.87	0.86	0.88	0.85	
	Lower		1.07	0.78	0.72	0.73	0.76	
	Maximum Daily Average							
	Upper		9.6	7.2	7.1	7.2	7.1	
	Lower		7.4	5.5	5.2	5.2	5.5	
	Maximum 1 hour Average							
	Upper		22.5	16.4	16.4	16.4	16.4	
	Lower		11.6	8.4	7.4	7.4	8.4	
1,3 Butadiene, ppb								
	Population Weighted Annual Exposure							
	Upper		0.36	0.20	0.21	0.20	0.21	
	Lower		0.34	0.19	0.19	0.19	0.20	
	Maximum Daily Average							
	Upper		2.9	2.9	2.9	2.9	2.9	
	Lower		2.0	2.0	2.0	2.0	2.0	
	Maximum 1 hour Average							
	Upper		6.8	6.8	6.8	6.8	6.8	
	Lower		3.1	3.1	3.1	3.1	3.1	
Acetaldehyde, ppb								
	Population Weighted Annual Exposure							
	Upper		1.8	1.5	1.6	1.8	1.5	
	Lower		1.8	1.5	1.5	1.7	1.5	
	Maximum Daily Average							
	Upper		6.2	6.2	6.2	6.2	6.2	
	Lower		5.1	5.1	5.1	5.1	5.1	
	Maximum 1 hour Average							
	Upper		17.7	16.7	16.9	17.1	16.9	
	Lower		13.8	13.1	13.2	13.4	13.2	
Formaldehyde, ppb								
	Population Weighted Annual Exposure							
	Upper		4.7	3.7	3.7	3.7	3.7	
	Lower		4.7	3.6	3.6	3.6	3.6	
	Maximum Daily Average							
	Upper		14.0	12.2	12.2	12.2	12.2	
	Lower		14.0	12.2	12.0	12.1	12.2	
	Maximum 1 hour Average							
	Upper		37.8	38.5	38.0	38.1	38.0	
	Lower		20.3	20.7	20.4	20.5	20.4	

Carbon Monoxide, ppm								
	Maximum 8 hour Average							
	Best	17.5	14.3	14.3	13.4	14.7		
	Maximum 1 hour Average							
	Best	22.5	19.2	19.2	18.0	19.7		
Nitrogen Dioxide, ppm								
	Maximum Annual Average Exposure							
	Best	0.043	Not estimated since no significant change in Max 1 hour					
	Maximum Daily Average							
	Best	0.117	0.098	0.097	0.097	0.097		
	Maximum 1 hour Average							
	Best	0.255	0.235	0.235	0.235	0.235		
Ozone, ppm								
	Maximum 8 hour Average							
	Best	0.206	0.196	0.197	0.196	0.198		
	Maximum 1 hour Average							
	Best	0.244	0.231	0.232	0.229	0.234		
Particulate Matter (10: or less), : g/m³								
	Maximum Annual Geometric Mean							
	Best	56	No significant change expected among 2003 scenarios					
	Maximum Daily Average							
	Best	227	No significant change expected among 2003 scenarios					
Ethanol, ppb (Estimated from Summer Measurements)								
	Population Weighted Annual Exposure							
	Upper	5.4	5.1	8.2	11.3	5.1		
	Lower	5.4	5.1	7.0	8.8	5.1		
	Maximum Daily Average							
	Upper	51	46	48	50	46		
	Lower	47	43	44	45	43		
	Maximum 1 hour Average							
	Upper	108	98	101	103	98		
	Lower	78	71	72	73	71		
MTBE, ppb								
	Population Weighted Annual Exposure							
	Upper	3.9	2.7	0	0	0		
	Lower	3.6	2.5	0	0	0		
	Maximum Daily Average							
	Upper	29	21	0	0	0		
	Lower	13	9	0	0	0		
	Maximum 1 hour Average							
	Upper	68	47	0	0	0		
	Lower	19	13	0	0	0		

PAN, ppb (Model Output Only)								
	Maximum Daily Average							
		Model	2.1	2.1	2.1	2.1	2.1	
	Maximum 1 hour Average							
		Model	4.4	4.2	4.4	4.4	4.4	
PPN, ppb (Model Output Only)								
	Maximum Daily Average							
		Model	0.6	0.6	0.6	0.6	0.6	
	Maximum 1 hour Average							
		Model	1.4	1.4	1.4	1.4	1.5	

